

NaNO₂/FeCl₃ dioxygen recyclable activator: An efficient approach to active oxygen species for degradation of a broad range of organic dye pollutants in water

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Abstract

A combination of ferric chloride and sodium nitrite is a competent catalyst for catalytic bleaching of a broad range of dye pollutants under moderate condition ($T = 150\text{ }^{\circ}\text{C}$; oxygen pressure = 0.5 MPa; pH 2.5). To evaluate the catalytic degradation system, we implemented wet oxidation of Acid Blue 129 (AB129) at the temperatures between 110 and 150 $^{\circ}\text{C}$ using FeCl₃/NaNO₂ as the catalyst. The degradation process was monitored by UV–vis spectroscopy, HPLC, IC, GC–MS and TOC analysis. At 150 $^{\circ}\text{C}$ and 0.5 MPa oxygen, 50.9% TOC and 100% color were removed after 2 h treatment, while no obvious TOC and only 20.4% color removal were achieved without the catalyst at the same experimental conditions. The main degradation products detected were CO₂ and some small organic acids. The reaction kinetics of the process was also studied in the temperature range of 120–150 $^{\circ}\text{C}$. AB129 degradation can be described by pseudo-first-order kinetics over the temperature range. Furthermore, this catalytic system is also highly efficient for tackling a variety of substrates including azo and anthraquinone dye pollutants.

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1. Introduction

The textile industries are becoming a major source of environmental contamination because an alarming amount of dye pollutants are generated during the dyeing processes [1]. In fact, about 700 000 tonnes of different dyes are produced annually in the world, among which about 50 000 tonnes of dyes are discharged into the environment [2]. In China, over $1.6 \times 10^9\text{ m}^3$ of dye-containing wastewater per year is drained into environmental water system without having been properly treated. Furthermore, one of the most marked features of modern dyes is their high degree of chemical, photolytic, and microbiological stability. Thus dyes are not readily degradable under aerobic conditions prevailing in the conventional

biological treatment processes [3–5]. And other conventional treatment technologies such as chemical coagulation, activated carbon adsorption, electrochemical treatment and reverse osmosis are usually inefficient in treating those dye pollutants [6]. Therefore, it is greatly needed to develop practical and highly efficient technologies for treatment of dye-containing wastewater.

In the last decades, oxidative degradation methods aiming at treating persistent organic pollutants in industrial wastewaters as versatile strategies have been actively explored [7–9]. From an economical and environmental viewpoint, the pursuit of using molecular oxygen (or air) as the terminal-oxidizing agent constitutes a highly attractive target for oxidative degradation of pollutants [10]. Wet oxidation (WO) is considered as one of the most promising and efficient techniques for degrading the pollutants to CO₂/CO or more biologically amenable intermediates [11]. Thus a large number of wet oxidation methods for the degradation of environmental pollutants have been developed [7,12–16]. The typical conditions of industrial

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operation of WO are high temperature (200–320 °C) and high pressure (2–20 MPa), which adversely affect the cost benefit ratio of the wet oxidation process [11,17]. Attempting to reduce the harsh process conditions, catalytic wet oxidation (CWO) has been studied extensively and numerous catalysts have been developed. Several research groups have studied the CWO of dyeing and printing wastewater and obtained some encouraging results [18–26]. Among these catalyst systems, copper salts were the most active homogeneous catalysts, but their use required a separation step to remove the toxic copper ion from the final effluent [27,28]. This drawback can be overcome by using heterogeneous catalysts which are easily retrievable and reused [18]. However, these heterogeneous catalysts, in many cases, are easily deactivated by sintering, poisoning or fouling [13,27]. Also, in hot acidic environments, the active components may dissolve into the liquid phase which is potentially toxic to the environment [13]. On the other hand, the degradation methods mainly focused on the treatment of azo dye pollutants, little information about CWO of the anthraquinone dyes was offered. Based on the above discussion, we sought to envisage and develop an innovative and inexpensive treatment method for a wide range of dye pollutants including anthraquinone dyes that would inherently facilitate industrialization. Specifically, we centered our attention on finding a catalytic system that utilizes inexpensive and readily available metal which is greener than copper as the catalyst, and cheap auxiliary agents as the co-catalyst. As such, one key feature is the catalytic system being effective for a broad range of dye pollutants at a wide pH range. Here we disclose that a combined catalyst of sodium nitrite and ferric chloride can preliminarily achieve these goals.

2. Experimental

2.1. Materials and reagents

Acid Blue 129 (AB129) was purified by the well-known *N,N*-dimethylformamide–acetone method [29]. All the other acid dyes (Hangzhou Xiasa Hengsheng Chemical Co. Ltd., China) and reactive dyes (Shanghai Matex Chemicals Co. Ltd., China) were used without further purification. HCl, NaOH, NaCl, NaNO₂, Na₂SO₄, FeCl₃·6H₂O, methanol and diethyl ether were of analytical grade and used without further purification. 0.2 M Me₃S⁺OH[−] methanol solution (Tokyo Kasei Kogyo Co. Ltd., Japan) was purchased from Acros. Water was prepared with a Milli-Q water purification system (Millipore, Milford, MA) throughout all the experiments. The pH values were adjusted by addition of diluted aqueous solutions of HCl or NaOH.

2.2. Degradation experiments

The CWO of AB129 was carried out in a 50 mL of Teflon-lined stainless steel autoclave equipped with a magnetic stirrer. The reaction temperature was measured using a thermocouple and controlled by a PID regulator. AB129 solution (20 mL, 0.22 mM, pH 2.5, adjusted with 2 M HCl), FeCl₃ (22 μL,

0.04 M) and NaNO₂ (22 μL, 0.20 M) were added to the autoclave, thus, the mole ratio of FeCl₃:NaNO₂:AB129 was 0.2:1:1. The autoclave was then closed and charged with pure oxygen to 0.5 MPa and then heated to the desired temperature. The stirring speed was set at 500 rpm. After reaction (heating time included), the autoclave was cooled to room temperature with a water bath. Carefully depressurized and sampled for further analysis. The experiments of other dyes were similar as described above. The kinetic experiments were carried out in the 5-L Hastelloy autoclave. The autoclave was charged with 3 L AB129 solution (0.22 mM, pH 2.5, adjusted with 3 M HCl), and the air in the reactor was purged with pure nitrogen for three times before nitrogen pressure of 0.5 MPa was maintained. Thereafter, the reactor was heated to the desired reaction temperature. Once the temperature was reached, 50 mL FeCl₃ solution (2.62 mM) and 50 mL NaNO₂ solution (13.09 mM) were immediately pumped into the reactor. Then 1 MPa pure oxygen (at a reference temperature of 25 °C) was supplied to the reactor and the time was considered to be “zero” for a reaction. The stirred speed was set at 600 rpm to ensure vigorous mixing, and the oxidation rate was not controlled by mass transfer effect. Samples were periodically withdrawn and analyzed for AB129 concentration and TOC. In the entire process, the system was kept under isobaric and isothermal conditions.

2.3. Analyses

The concentration of the dyes was determined using UV–vis spectrophotometer (Jasco V550) at the maximum wavelength of the dyes studied. The color removal was based on the change of the maximum absorbance. GC–MS analysis was performed on an Agilent 6890/5973 GC–MS instrument equipped with a Varian VF-5 ms capillary column (60 m × 0.25 mm × 0.25 μm). The carrier gas was helium and the voltage of electron impact ionization was 70 eV. The temperature program of the column was set as follows: at 60 °C, hold time = 5 min; from 60 to 180 °C, rate = 5 °C/min; from 180 to 250 °C, rate = 10 °C/min; at 250 °C, hold time = 10 min. The sample for GC–MS analysis was prepared as follows: after 4-h reaction of AB129 (0.44 mM) under 0.5 MPa dioxygen and 150 °C, the aqueous solution (20 mL) was withdrawn. The water was removed under vacuum leaving a pale yellow residue. The residue was dissolved in sufficient 3 M HCl to produce a pH < 2 solution. The resulting solution was saturated with NaCl and extracted with diethyl ether (3 × 10 mL). The combined ether extracts were dried with anhydrous sodium sulfate and ether was evaporated under vacuum. The residue was dissolved in 1 mL methanol, and 0.5 mL 0.2 M Me₃S⁺OH[−] in methanol was added to the methanol product solution before GC–MS analysis. Inorganic anions and small molecular organic acids were identified and evaluated by means of ion chromatography (Dionex 2500), equipped with an AS 11-HC anion separator column (250 mm × 4 mm) and an ED-50 electrochemical detector operating in conductivity mode. The suppressor current was 30 mA. The eluent was 10 mM aqueous NaOH solution and the flow rate was 1.2 mL/min. The total

organic carbon (TOC) was measured via a Shimadzu 5050 TOC analyzer.

3. Results and discussion

3.1. CWO of AB129

We have recently developed a novel catalyst (sodium nitrite), which showed a high catalytic activity for the aerobic oxidative degradation of trichlorophenol, a kind of persistent environmental pollutant [30]. Attempting to extend the oxidative degradation methodology, we designed the NaNO_2 -based aerobic oxidative degradation system for anthraquinone dye pollutants. AB129 (the molecular structure is shown in Fig. 1) was used as a prototypical pollutant to examine its degradation in such a system. The initial experiments were carried out with sole NaNO_2 as the catalyst. Unfortunately, despite extensive efforts, AB129 remained recalcitrant toward the degradation method. For example, when 100 mol% NaNO_2 (corresponding to 1:1 mol ratio of NaNO_2 to AB129) was reacted with AB129 for 2 h in the presence of 0.5 MPa dioxygen at 150 °C, the color of reaction mixture turned into purple, yet the total organic carbon (TOC) remained invariable. Prolonging the reaction time and increasing the use amount of NaNO_2 and/or increasing dioxygen pressure did not lead to obvious improvement of the reaction results. These results clearly indicated that the catalytic activity of NaNO_2 was not high enough to thoroughly destroy AB129. Thus it needed a co-catalyst to promote the overall catalytic activity of NaNO_2 . Homogeneous iron salts in WO systems have been reported to be effective catalysts for enhancing the destruction of phenol [31]. Recently, our investigation demonstrated that the incorporation of FeCl_3 into NaNO_2 could catalytically activate molecular oxygen for selective oxidation of alcohols [32]. Very recently, we disclosed that a combination of FeCl_3 and NaNO_2 could lead to efficient photocatalytic degradation of the steroid estrogens under natural light irradiation [33]. Most notably, iron is an extremely abundant and cheap metal and greener than copper. With these in mind, we envisioned that FeCl_3 might be an ideal mate to NaNO_2 toward structure a cheap and green catalyst system for efficient oxidative degradation of organic dye pollutants using molecular oxygen as the oxidizing agent. Indeed, when 20 mol% FeCl_3 (corresponding to 0.2:1 mol ratio of FeCl_3 to AB129) and 60 mol% NaNO_2 were used, we found that the color of the reaction mixture was bleached and the TOC decreased 38.5%

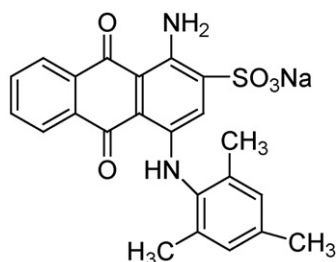


Fig. 1. The structure of AB129.

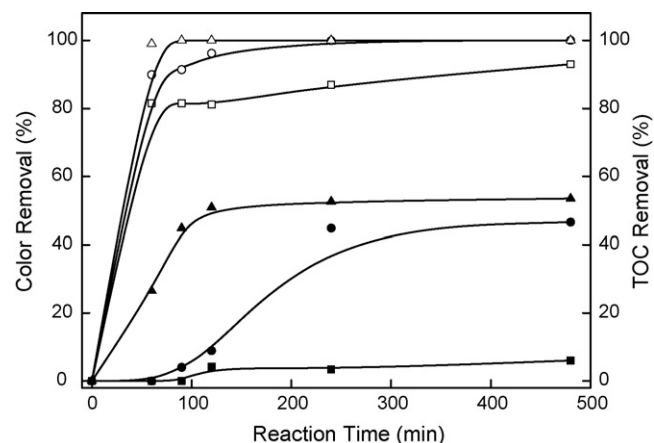


Fig. 2. Influence of temperature on color and TOC removal of AB129. Experimental conditions: pressure = 0.5 MPa; [AB129] = 100 mg/L (0.22 mM); the mole ratio of FeCl_3 : NaNO_2 :AB129 = 0.2:1:1; pH 2.5. (□) Color removal at 110 °C; (○) color removal at 130 °C; (Δ) color removal at 150 °C; (■) TOC removal at 110 °C; (●) TOC removal at 130 °C; (▲) TOC removal at 150 °C.

after 2 h of reaction under 0.5 MPa dioxygen at 150 °C. To further elucidate the characteristics of the newly developed degradation process, TOC removal versus reaction time profile was measured (Fig. 2). As shown in Fig. 2, a rapid TOC removal rate is observed at initial reaction period, and then the reaction rate goes to slow. For example, more than 44.8% TOC removal is achieved after 90 min of reaction at 150 °C. However, prolonging the reaction time to 8 h, the TOC removal only added 8.7% (44.8–53.5%). The UV–vis spectral changes taking place during the CWO of AB129 mediated by FeCl_3 / NaNO_2 are displayed in Fig. 3. The characteristic absorption bands of AB129 at approximately 628 and 592 nm rapidly disappeared with a new absorption band at approximately 467 nm occurred within 1 h of reaction. Concomitantly, the color of the reaction solution changed from the initial blue to light red. As the reaction time further prolonged, the visible absorption band completely disappeared and the solution was

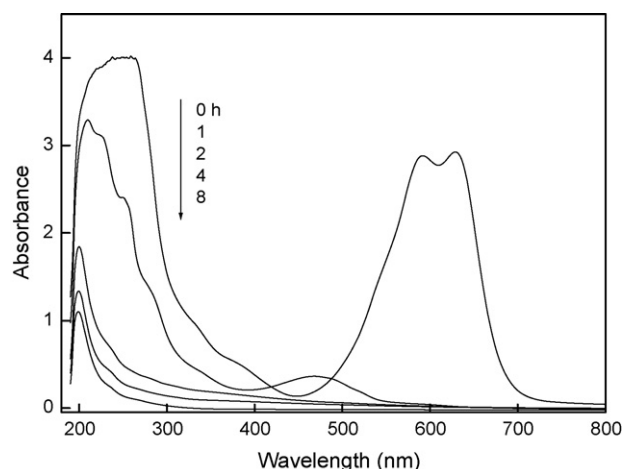


Fig. 3. UV–vis spectral changes of AB129 with reaction time. Experimental conditions: temperature = 150 °C; pressure = 0.5 MPa; [AB129] = 100 mg/L (0.22 mM); the mole ratio of FeCl_3 : NaNO_2 :AB129 = 0.2:1:1; pH 2.5.

totally discolored. This indicated that the chromophoric structure of AB129 was completely destroyed. In view of these results, we systematically investigated and optimized the reaction conditions (temperature, oxygen pressure, pH and use amount of NaNO_2 and FeCl_3).

3.2. Effect of temperature

Temperature is an extremely important factor in the WO process. One key criterion for evaluation of a CWO system is reduction extent of the reaction temperature because low reaction temperature could intrinsically lower the barrier of industrialization. The oxidation of AB129 has been studied at temperatures ranging from 110 to 150 °C and 0.5 MPa oxygen pressure. The result shown in Fig. 2 suggests 50.9% TOC and 100% color removal were achieved at 150 °C within 2 h of reaction. Furthermore, a control experiment indicated that the oxidative degradation of AB129 was totally ineffective in the absence of FeCl_3 and NaNO_2 . In order to further explore the potential of the catalyst system, we carried out the experiments at lower reaction temperatures. For example, when the reaction temperature was lowered to 130 °C, no obvious difference in color removal was observed compared with that at 150 °C. Interestingly, when the reaction temperature was further lowered to 110 °C, there were still 6% TOC removal and 93% color fading within 8 h. These results clearly demonstrated that the degradation system remained efficient at a relatively low reaction temperature such as 110 °C.

3.3. Effect of amount of NaNO_2 and FeCl_3

To understand the role of NaNO_2 and FeCl_3 in the present degradation system, experiments with various use amounts of NaNO_2 and FeCl_3 were accomplished. As shown in Fig. 4, there is only 53.8% color and no TOC removal of AB129 in the presence of 20 mol% FeCl_3 alone for 2 h of reaction. When the amount of FeCl_3 was fixed at 20 mol%, and the reaction time was set at 2 h, the addition of NaNO_2 obviously improved the

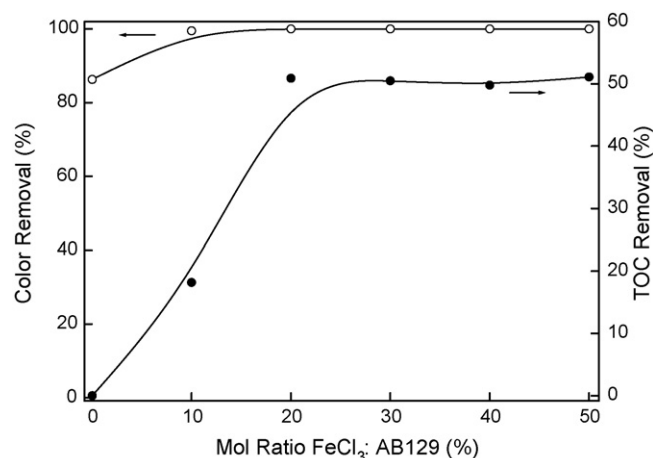


Fig. 5. Influence of FeCl_3 amount on color and TOC removal of AB129. Experimental conditions: temperature = 150 °C; pressure = 0.5 MPa; time = 2 h; $[\text{AB129}] = 100 \text{ mg/L}$ (0.22 mM); the mole ratio of NaNO_2 :AB129 = 1:1; pH 2.5. (○) Color removal; (●) TOC removal.

destruction of AB129. For example, when using 20 mol% NaNO_2 , color removal was up to 78%, although there was no significant improvement in TOC removal. Increasing the NaNO_2 amount to 60 mol% led to 100% color and 38.5% TOC removal. Further increasing the NaNO_2 amount to 80 mol% obtained 50.9% TOC removal. However, when the NaNO_2 amount was increased to 100 mol%, there was no further improvement in TOC removal compared with that at 80 mol% NaNO_2 . The results indicated that 80 mol% might be an ideal dosage for NaNO_2 use in current degradation system for AB129.

Fig. 5 shows the effect of FeCl_3 amount on the color and TOC removal of AB129 in the presence of 100 mol% NaNO_2 . The addition of FeCl_3 to the NaNO_2 catalytic system has a significant effect on the degradation of AB129. The control experiment showed that only by using 100 mol% NaNO_2 , 86.3% color was removed but TOC remained unchanged. With the addition of 10 mol% FeCl_3 , the color and TOC removal increased to 99.5% and 18.2%, respectively. When the FeCl_3 amount was increased from 10 to 20 mol%, there was a 42.7% (18.2–50.9%) improvement in TOC removal and color removal attained 100%. Further increasing the FeCl_3 amount to 50 mol% did not lead to obvious improvement in TOC removal. The results indicate that the 20 mol% is sufficient amount for FeCl_3 in the present system.

In present cases, we postulate that NO_2/NO , $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ and ONOO^- are most likely to be involved in the present catalytic system. Peroxynitrite, which has oxidative activity similar to a hydroxyl radical, and Fe^{III} might act as the most important active oxidants for the degradation of dye pollutants. Acidifying NaNO_2 with HCl generates NO and NO_2 . It is known that O_2^- , an ever-present concurrent species in many Fe-based aerobic oxidation reactions which was formed by the one-electron reduction of dioxygen (Eq. (1)), reacts extremely easily with NO to generate ONOO^- [34–40]. Peroxynitrite oxidized the pollutants resulting in generating degradation offspring and NO_2 . In addition, the oxidation of NO by

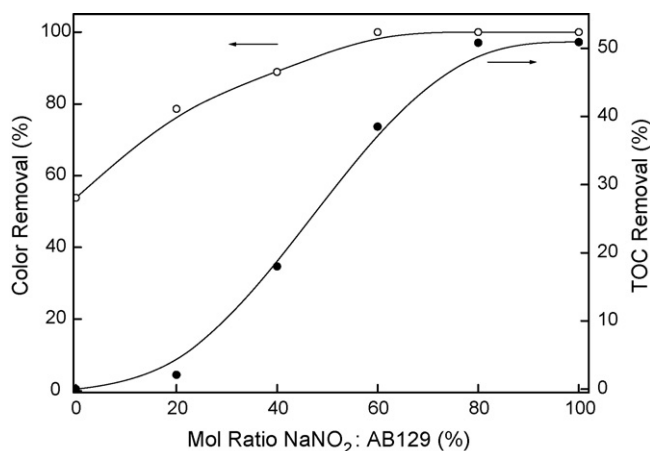


Fig. 4. Influence of NaNO_2 amount on color and TOC removal of AB129. Experimental conditions: temperature = 150 °C; pressure = 0.5 MPa; time = 2 h; $[\text{AB129}] = 100 \text{ mg/L}$ (0.22 mM); the mole ratio of FeCl_3 :AB129 = 0.2:1; pH 2.5. (○) Color removal; (●) TOC removal.

dioxygen can generate NO_2 (Eq. (2)). While the NO_2 oxidized Fe^{II} to Fe^{III} , NO_2 itself was reduced to regenerate NO . The production of Fe^{II} arose because Fe^{III} was reduced by the pollutants or some reductive intermediate products. In fact, our experiments demonstrated that FeCl_2 worked just as well as FeCl_3 in present degradation system. When the reductive intermediate products at last were converted to CO_2/CO or the products which could not further reduce Fe^{III} to Fe^{II} , NO was finally oxidized to NO_3^- by dioxygen.



3.4. Effect of oxygen pressure

The oxygen pressure is also an important factor toward the aerobic oxidative degradation system for environmental pollutants [41–44]. The effect might be related to the oxygen concentration in the liquid phase. According to the Henry's law, the concentration of O_2 dissolved in the liquid phase is proportional to the partial pressure of O_2 in the gas phase. Therefore, an increase in the oxygen pressure in gas phase will enhance the dissolved oxygen concentration in the liquid phase which is beneficial to the pollutant oxidation. To investigate the effect of oxygen pressure on the present CWO of AB129, five experiments were conducted at pressures ranging from 0.1 to 0.5 MPa. Fig. 6 shows that the color and TOC removal increases with the oxygen pressure increasing. However, the effect was only noticeable when the oxygen pressure increased from 0.1 to 0.4 MPa, the difference between 0.4 and 0.5 MPa was somewhat insignificant. This may be because the oxygen pressure above 0.4 MPa, CWO of AB129 transforms from the oxygen diffusion control to reaction control. The oxygen pressure of 0.4 MPa was thus considered to be sufficient in the present system.

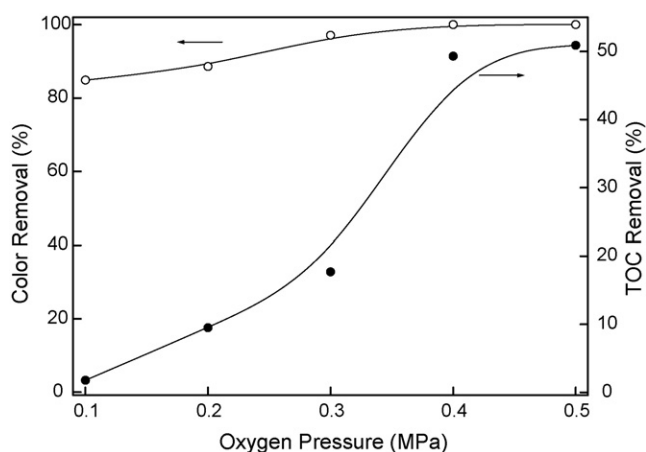


Fig. 6. Influence of oxygen pressure on color and TOC removal of AB129. Experimental conditions: temperature = 150 °C; time = 2 h; [AB129] = 100 mg/L (0.22 mM); the mole ratio of $\text{FeCl}_3\text{:NaNO}_2\text{:AB129} = 0.2\text{:}1\text{:}1$; pH 2.5. (○) Color removal; (●) TOC removal.

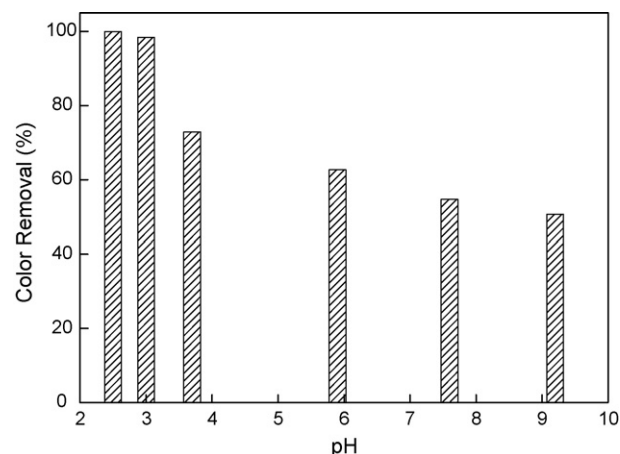


Fig. 7. Influence of pH on color removal of AB129. Experimental conditions: temperature = 150 °C; pressure = 0.5 MPa; time = 2 h; [AB129] = 100 mg/L (0.22 mM); the mole ratio of $\text{FeCl}_3\text{:NaNO}_2\text{:AB129} = 0.2\text{:}1\text{:}1$.

3.5. Effect of pH

Since solution pH has been reported to have a significant effect on the WO of organic compounds [13], the WO of AB129 was investigated at various pH values in the $\text{FeCl}_3/\text{NaNO}_2$ system (Fig. 7). Clearly, the reaction could occur at such a wide pH range from 2.5 to 9.2. Although the color removal was decreased with the increase in initial pH, 50.7% color removal was still achieved when the pH was at 9.2. However, the TOC removal was rapidly decreased with initial pH increasing. For example, TOC decreased 50.9% at pH 2.5 while 17.4% at pH 3.0, and no obvious TOC removal was observed at pH higher than 3.0. This tendency may be due to the precipitation of Fe^{3+} into amorphous oxyhydroxide complexes, which becomes rapid above pH 3.0 [45–51], decreasing the Fe^{3+} concentration in solution.

3.6. Reaction kinetics

To gain a better insight into the process, the kinetics of AB129 CWO were investigated in the temperature range of 120–150 °C, at 1 MPa oxygen partial pressure. In all cases, the initial oxygen concentration was fixed at a great excess over the stoichiometric concentration needed to the complete AB129 oxidation to CO_2 and H_2O , so it was possible to approximate the expression to pseudo-first order, given by the following equation:

$$-\ln \frac{[\text{AB129}]}{[\text{AB129}]_0} = k'_{\text{AB129}} t \quad \text{or} \quad -\ln \frac{[\text{TOC}]}{[\text{TOC}]_0} = k'_{\text{TOC}} t$$

and

$$k' = A \exp \left(-\frac{E_a}{RT} \right)$$

For all the runs, a pseudo-first-order kinetic fit is obtained (Fig. 8). The values of kinetic constants (k'_{AB129} and k'_{TOC}) obtained by linear regression of the model were listed in

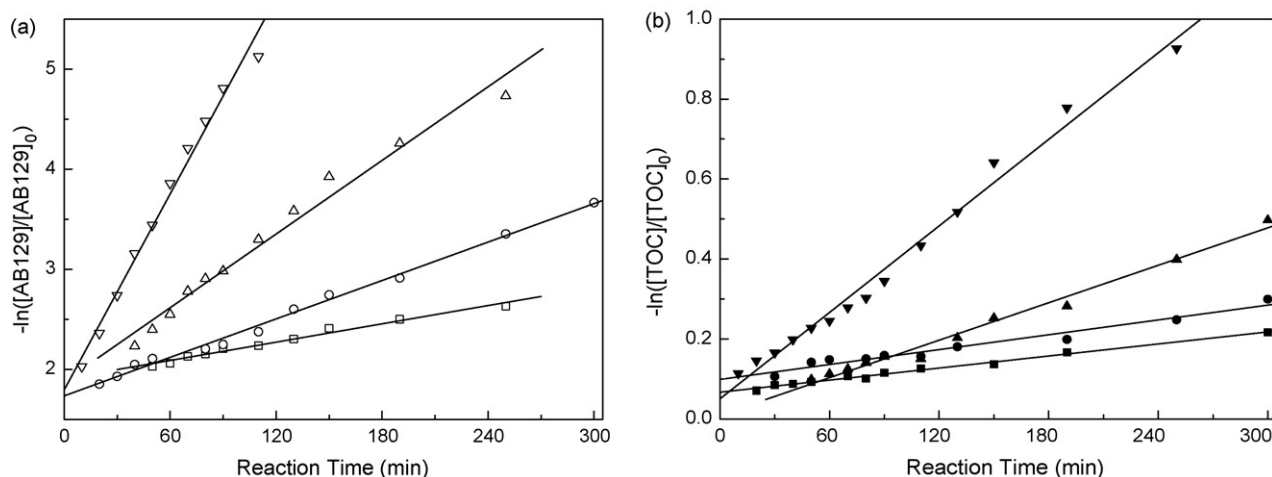


Fig. 8. AB129 catalytic wet oxidation fitting to pseudo-first-order kinetics at different temperatures. Experimental conditions: pressure = 1.0 MPa; [AB129] = 100 mg/L (0.22 mM); the mole ratio of $\text{FeCl}_3\text{:NaNO}_2\text{:AB129} = 0.2\text{:}1\text{:}1$; pH 2.5. (a) (□) 120 °C; (○) 130 °C; (Δ) 140 °C; (▽) 150 °C. (b) (■) 120 °C; (●) 130 °C; (▲) 140 °C; (▼) 150 °C.

Table 1. As can be seen that both k'_{AB129} and k'_{TOC} increases with increasing temperature, but k'_{TOC} is significantly lower than k'_{AB129} at the same temperature, due to the fact that the intermediate products such as formic, acetic, pyruvic acid, etc. formed during the course of AB129 oxidation are more stable to further oxidation. Assuming that k' follows an Arrhenius-type behavior, the activation energy, E_a can be calculated by performing a linear fit of $\ln k'$ versus $1/T$, as shown in Fig. 9. The activation energy for AB129 degradation was found to be 106.4 kJ/mol ($r^2 = 0.988$) whereas a value of E_a for TOC destruction was 95.0 kJ/mol ($r^2 = 0.934$).

3.7. Mineralization of AB129

The extent of mineralization is also one of the most important factors to evaluate a new oxidative degradation system. We determined and quantified both the SO_4^{2-} released and the residual TOC. The amount of SO_4^{2-} generated was measured by ion chromatography. As shown in Fig. 10, sulfur mineralization is ca. 92% after 4 h at 150 °C. Moreover, most SO_4^{2-} is formed after 2-h reaction. This indicated sulfonic group removal was a relatively fast-reaction process. TOC measurements indicated that 53.5% of the carbon in AB129 was mineralized after 8 h at 150 °C. These analyses demonstrated that AB129 was nearly completely destroyed and a considerable amount was mineralized; only a fraction of the AB129 was converted into lower organic products (Fig. 11).

Table 1
Pseudo-first-order kinetic constants and correlation coefficients in AB129 catalytic wet oxidation

T (°C)	k'_{AB129} (min^{-1})	r^2	k'_{TOC} (min^{-1})	r^2
120	0.0031	0.9821	0.0005	0.9892
130	0.0064	0.9926	0.0006	0.9610
140	0.0122	0.9835	0.0016	0.9859
150	0.0326	0.9872	0.0036	0.9880

The mass balance was determined by the mineralization of organic carbon and some measurable reaction products by ion chromatography analysis. The fate of 87.2% of the carbon atoms is accounted for 8-h reaction (Table 2).

3.8. Identification of reaction products of AB129

The reaction products were identified and quantified with known standards by ion chromatography. The results showed that measurable reaction products mainly contained acetic acid (1), formic acid (2), pyruvic acid (3) and succinic acid (4) (Fig. 11). GC–MS was used to identify other residual organic compounds and the results revealed that the major product was phthalic acid (12), and other detectable minor components included glycolic acid (6), lactic acid (7), fumaric acid (8),

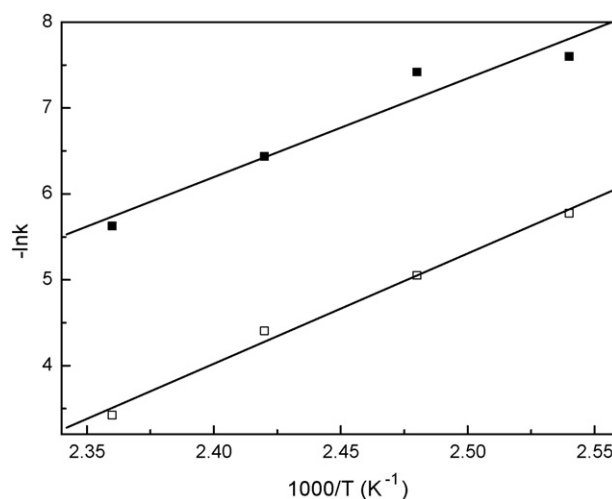


Fig. 9. Effect of temperature on kinetic constants of AB129 catalytic wet oxidation. Experimental conditions: pressure = 1.0 MPa; [AB129] = 100 mg/L (0.22 mM); the mole ratio of $\text{FeCl}_3\text{:NaNO}_2\text{:AB129} = 0.2\text{:}1\text{:}1$; pH 2.5. (□) AB129 degradation; (■) TOC removal.

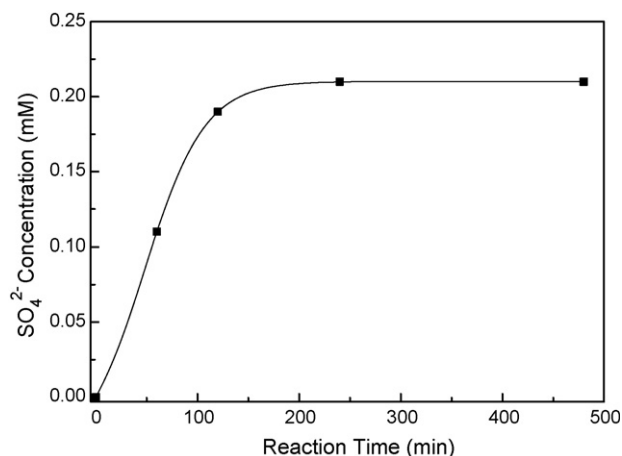


Fig. 10. Sulfate ion released after AB129 catalytic wet oxidation degradation. Experimental conditions: temperature = 150 °C; pressure = 0.5 MPa; [AB129] = 100 mg/L (0.22 mM); the mole ratio of FeCl₃:NaNO₂:AB129 = 0.2:1:1.

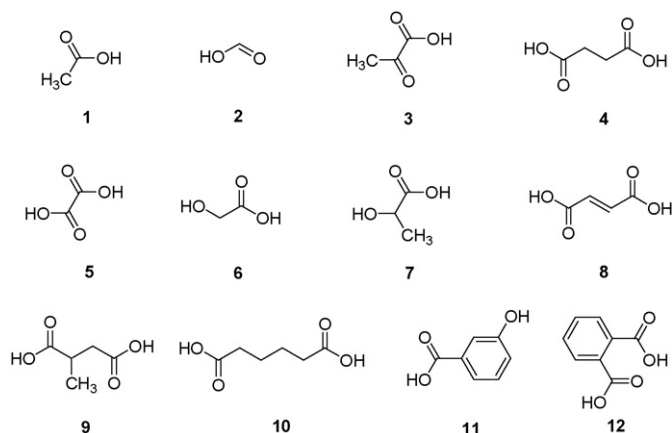


Fig. 11. Products formed after AB129 degradation by NaNO₂/FeCl₃-catalyzed oxidation.

2-methylsuccinic acid (9), hexanedioic acid (10), 3-hydroxybenzoic acid (11) (Fig. 11). These results indicated that the most detectable degradation products were mainly small molecular organic acids, which are known to be biologically degradable.

Table 2
Mass balance after the degradation of AB129

Compound	1 h		2 h		4 h		8 h	
	mM	% C	mM	% C	mM	% C	mM	% C
C + CO ₂		26.5		50.9		52.6		53.5
Acetic acid	0.22	8.8	0.54	21.5	0.54	21.5	0.57	22.7
Formic acid	0.14	2.8	0.44	8.8	0.45	9.0	0.47	9.4
Pyruvic acid	0.07	4.2	0.03	1.8	0.02	1.2	n.d.	n.d.
Succinic acid	n.d.	n.d.	0.02	1.6	0.02	1.6	0.02	1.6
Oxalic acid	0.01	0.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total	42.7		84.6		85.9		87.2	

n.d. = not detected.

Table 3

Oxidation of other dyes with NaNO₂/FeCl₃ and oxygen under different reaction conditions^a

Entry	Dye	Decoloration of dye (%)	Removal of TOC (%)
1	Acid Blue 25	99.9	60.9
2	Acid Blue 40	100	61.3
3	Acid Blue 41	100	61.9
4	Acid Blue 45	100	68.0
5	Acid Blue 62	100	46.3
6	Acid Blue 80	100	39.3
7	Acid Blue 140	100	28.7
8	Acid Blue 182	100	35.9
9	Acid Blue 225	100	35.5
10	Acid Blue 277	100	48.4
11	Acid Violet 43	100	54.7
12	Acid Violet 48	100	47.9
13	Acid Green 25	100	41.1
14	Acid Green 27	100	46.2
15	Acid Green 28	100	43.9
16	Reactive Orange 122	100	39.5
17	Reactive Red 222	100	24.0
18	Reactive Red 241	100	28.4
19	Reactive Yellow 145	100	22.1
20	Reactive Blue 194	100	14.7
21	Reactive Blue 222	100	35.8
22	Reactive Black 5	100	22.4
23 ^b	Acid Orange 7	100	35.8

^a Experimental conditions: dye stock solution (200 mg/L, 20 mL, pH 2.5) was treated with NaNO₂/FeCl₃ and oxygen in the 50-mL Teflon-lined autoclave, FeCl₃:NaNO₂:dye mole ratio (0.2:1:1), temperature (150 °C), oxygen pressure (0.5 MPa), time (4 h).

^b Dye solution (100 mg/L, 20 mL, pH 2.5) was treated.

3.9. Degradation of other dyes

The substrate scope is one of the critical factors for the evaluation of new oxidative degradation system. Thus one key requisite for an ideal oxidative degradation method of organic dye pollutants is the catalyst being useful for tackling a variety of dye pollutants. The reaction condition was later applied to the aerobic oxidation degradation of a variety of prototypical dye pollutants. The scope of the method is illustrated (Table 3) by the wide range of both azo and anthraquinone dyes that can be removed in a full degree of decoloration. For example, with 100 mol% NaNO₂ and 20 mol% FeCl₃ at 150 °C and 0.5 MPa

of O₂, all azo dyes employed (entries 16–23) were thoroughly discolored with a moderate mineralization of TOC. It is interesting to note that anthraquinone dyes (entries 1–15), which are generally believed to be the most recalcitrant to oxidative degradation in other reported wet oxidation protocols [52–54] were totally destroyed and their colors were completely bleached.

4. Conclusions

The FeCl₃/NaNO₂/O₂ system efficiently bleaches a broad range of organic dyes and oxidizes the substrates into CO₂ and biodegradable organic products with a high-conversion rate. To the best of our knowledge, such a broad range of organic dyes being bleached and relatively highly mineralized using dioxygen as the oxidant has not been reported previously. As such, the oxidative degradation method remains effective at a relatively wide pH range. Furthermore, the use of dioxygen as the oxidizing agent and FeCl₃/NaNO₂ as the catalyst renders the reaction is interesting from both economical and environmental points of view. Therefore, this inexpensive, simple and efficient catalytic degradation system facilitates its industrial applications.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcatb.2007.10.017.

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